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COMPATIBILITY OF CONTAMINANTS
AND PLASTICS WITH SOLVENTS

PDO 6984805, Topical Report

L. C. Jackson, Project Leader

Project Team:
E. T. Walsh

Internal Distribution March 1975

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Reference: Your Request for Lloyd Jackson's Report,
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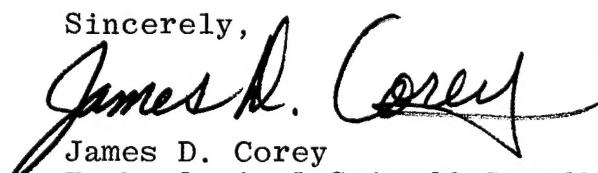
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AND PLASTICS WITH SOLVENTS**

Internal Distribution March 1975

Project Leader:
L. C. Jackson
Department 814

Project Team:
E. T. Walsh

PDO 6984805
Topical Report

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COMPATIBILITY OF CONTAMINANTS AND PLASTICS WITH SOLVENTS

BDX-613-1240 (Rev.)

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Prepared by L. C. Jackson, D/814, under PDO 6984805

Specific contaminants on plastics can be removed without damaging the plastics by using improved solvent selection techniques. The desired solvent or solvent blend can be selected by referring to established compatibility charts. The effectiveness of a particular solvent relates to a numerical value on the chart. Solvent blends are also included which may be used to remove more contaminants than only one solvent can. The charts were derived from a combination of solubility parameter technology and evaporative rate analysis. Alternate solvent selection is possible to replace solvents which are not exempt from federal regulations or solvents which may become unavailable.

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CONTENTS

Section	Page
SUMMARY	5
DISCUSSION	6
SCOPE AND PURPOSE.	6
ACTIVITY	6
<u>Description of Contaminants</u>	6
<u>Solubility Parameter Technology</u>	6
<u>Evaporative Rate Analysis</u>	8
<u>Solvents and Solvent Blends</u>	8
<u>Swell Index of Plastics</u>	10
ACCOMPLISHMENTS.	15
FUTURE WORK.	15
REFERENCES.	16
DISTRIBUTION.	17

ILLUSTRATIONS

Figure	Page
1 Solubility Parameter Solubility-Incompatibility Concept	7

TABLES

Number	Page
1 Effects of Solvents on Contaminants.	9
2 Solvent Blend Formulations	11
3 Effects of Solvent Blends on Contaminants.	12
4 Effects of Solvents on Plastics.	13
5 Effects of Solvent Blends on Plastics	14

SUMMARY

The use of solvents is being looked at very critically as a result of environmental improvement requirements being established by state and federal agencies. Although purchase cost is a factor in selecting alternate solvents for particular requirements, performance controls the process cost and the integrity of a bonded part. Good adhesion depends upon effective contaminant removal and this is done by solvents.

It is possible to characterize contaminants so that the exact solvent or solvents for an effective cleaning job can be known. To do this, solubility parameter technology and evaporative rate analysis techniques must be used. Accuracy in solvent selection for contaminant removal can be improved by classifying solvents into three groups of weak, moderate, and strong hydrogen bonding potential. Increased capability in contaminant removal can be obtained by select solvent blending utilizing solubility parameter values as a guide.

The solvents selected to remove contaminants must not dissolve the plastic or cause crazing of the surface. Solvent sensitivity of plastics can be determined by a swell index test.

Compatibility of contaminants-solvents-plastics and their inter-relationships can be ascertained from the charts presented.

DISCUSSION

SCOPE AND PURPOSE

This phase of the work establishes compatibility charts showing the relative solvency of contaminants and plastics by using solvent series and blends based on solubility parameter technology.

ACTIVITY

Description of Contaminants

The criteria for acceptable surface cleanliness in the past has been determined by satisfactory performance of electrical components or adhesion tests. However, unexplained failures with the more complex or densely-packed components now require that a more fundamental approach to contaminant removal be initiated.

In the area of surface cleanliness, the subject of organic contaminants is not sufficiently defined. Present technology does not address itself to definition or measurement of contaminants on parts. Selecting solvents for best removal of contaminants has basically been evaluated by trial and error methods.

Contaminants are usually unknown materials described generally as oil, grease, fingerprints, or solder flux. A contaminant, or organic residue, is an unwanted material which usually occurs on parts as a thin film or monomolecular layer. Dust particles are also contaminants, but they are not included in this discussion.

Previous work has described how specific contaminants can be characterized and effectively removed by proper choice of solvents.¹ Aside from the problems associated with reuse of contaminated solvents, solvency time factor, and drag-out effects; the individual use of solvents, one after the other, may not be effective enough if more than one contaminant is on a substrate. A solvent blend which would dissolve more contaminants would provide greater potential for contaminant removal and eliminate the difficulty of selecting the proper solvents in the correct sequence.

Solubility Parameter Technology

Solubility parameter technology involves the study of how compatible materials are with each other. Similar molecules

dissolve more easily in each other than do dissimilar molecules. When the solubility parameter of a material to be dissolved is known, it becomes the "target area" as shown in Figure 1. Selection of a solvent reasonably close to that (target's) solubility parameter will provide increased solubility. However, if a solvent is chosen that has a solubility parameter too far away from the target area, the molecules will not match of fit together, and there will be little diffusion, molecular attraction, or solubility.

The accuracy in selecting solvents for contaminant removal can be improved by utilizing the knowledge that molecules have different levels of activity which greatly influence compatibility. Classification of solvents into three groups of weak, moderate, and strong hydrogen bonding potential is very useful. It tends to group solvents according to their electron charge capability. The strong hydrogen bonders are the alcohols; these have high solubility parameter values. The weak hydrogen bonding solvents are chlorinated compounds and hydrocarbons such as heptane and toluene; they have low solubility parameter values. In between are the moderate hydrogen bonders such as esters and ketones.

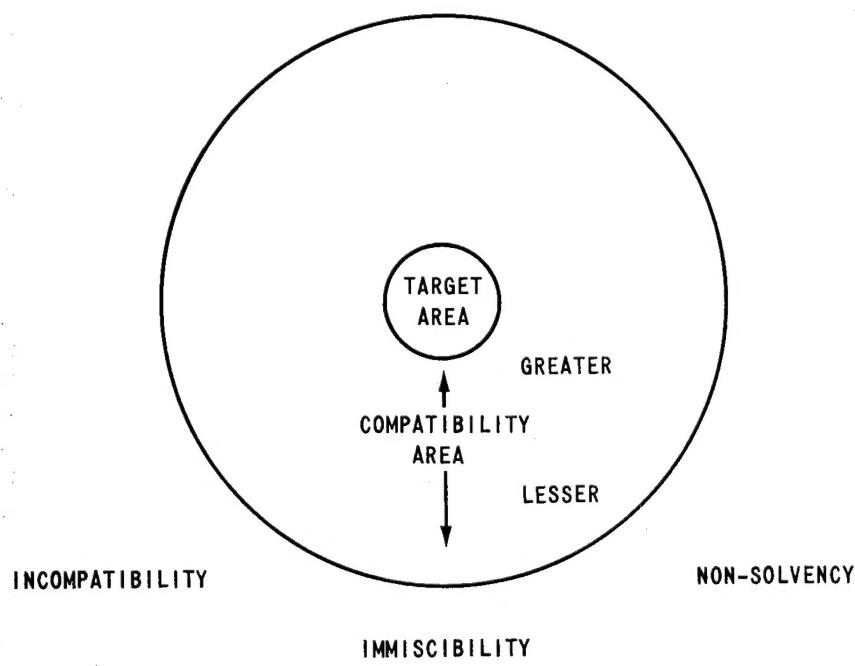


Figure 1. Solubility Parameter Solubility-Incompatibility Concept

Some contaminants like machine oil will only dissolve in some of the weak hydrogen bonding solvents. Photoresist, on the other hand, may only be dissolved by moderately hydrogen-bonding solvents. Other contaminants can be dissolved by solvents from both categories because their molecules have characteristics of each group.¹

Evaporative Rate Analysis

A few molecular layers of a contaminant on a surface cannot be seen and it has been difficult to detect their presence. Generally adhesion tests are used as final proof that contaminants have been removed. However, there has been evidence that adhesion values can hide the fact that contaminants were present on the surface at the time of bonding.² A more definitive method of determining the presence of contaminants was needed.

It is possible to determine whether or not a contaminant is present on a surface by a technique known as evaporative rate analysis.^{1, 2, 3} This method involves measuring the rate of evaporation of a carbon-14-tagged radioactive solvent from a surface by a means of a Geiger counter. The degree of retention of the radioactive solvent is a measure of contamination.

The Meseran Surface Analyzer (ERA Systems, Chattanooga, Tennessee) employs this principle and was used as a surface energy probe for this investigation.

Solvents and Solvent Blends

The capability of solvents to remove a variety of contaminants has been studied. Solvents were selected that represented a major portion of the solubility parameter range of 7 to 12. Each of the contaminants was individually rinsed in a flowing stream of the respective solvent under investigation. One hundred milliliters (1 dm³) of solvent was used for 60 seconds for each application. After each contaminant was rinsed, the level of radioactivity counts was determined using the Meseran Surface Analyzer for an interval of 112 seconds. The effectiveness of contaminant removal, as determined by the lowest Meseran values obtained is given in Table 1. Cleaning efficiency will be based on how close the solubility parameter value of the solvent is to the solubility parameter target area of the contaminant.

Since there is no solvent that will remove all contaminants, the practice has been to use 2 or 3 solvents, one after the other. It would be more desirable to have a formulation blend that had the potential of dissolving more contaminants than the individual solvents do. A blended solvent acquires the percentage average of the solubility parameter and polarity of the individual

Table 1. Effects of Solvents on Contaminants (Relative Ease of Removal of Contaminants, by Solvent Series)

Contaminants	Hep-tane	Hydrogen Bonding Class										Strong		
		2-Ethyl-hexyl-Chloride	Trichloro-trifluoro-ethane	Methyl-Chloro-form	Tol-uene	Tri-chloro-ethylene	Perchloro-ethylene	Methylene Chloride	Vinyl Tri-chloride	2-Ethyl-hexyl-Acetate	n-Butyl Acetate	Cellu-Solve-Acetate	Ace-tone	Cyclo-hexanone
Solder Flux Types														
• Abietic Acid	C	C	C	A	C	A	C	A	B	B	B	B	B	B
• Stearic Acid	C	C	A	C	A	A	A	A	A	B	B	C	C	A
Machine Oil	C	C	A	B	B	A	A	C	C	C	C	C	C	C
Photo Resist	C	C	C	C	C	C	C	C	C	A	B	B	A	C
Spray Coating	C	C	C	A	A	A	B	A	C	C	B	B	A	B
Fingerprint	B	A	A	A	B	A	A	B	B	B	A	B	A	A
Hand Lotion	B	A	A	B	A	A	A	C	A	A	C	C	C	C
Detergent	C	C	C	C	C	C	C	C	B	B	B	C	C	A
Mold Release (Carnauba Wax)	C	C	C	C	C	C	C	C	C	C	C	C	C	C
Grease	B	C	C	C	C	C	C	C	A	B	C	C	B	C
Silicone Grease	C	C	C	C	C	C	C	C	C	C	C	C	C	C

Levels of contaminants solubility based on Mescran (ERA Systems, Inc., Chattanooga, Tennessee) values after solvent rinsing.

*A = Contaminant effectively removed (16 or less Mescran units)

B = Partly soluble. Longer rinse times should improve contaminant removal (17 to 99 Mescran units)

C = Limited contaminant solubility in solvent (greater than 100 Mescran units)

components, and, therefore, a new entity. However, once the solubility parameter and polarity of a solvent have been varied because of a blending operation, there is no guarantee that the original contaminant removal capability of the individual solvents will be retained.

A series of solvent blends was formulated to provide polarity and solubility parameter composites which represented areas not covered by the individual weak, moderate, and strong hydrogen bonding solvents. The formulations are given in Table 2. Their contaminant removal capability is shown in Table 3. The effect on plastics is given in Table 5. Selection of solvents can be made depending upon the type of contaminant that must be removed. Solvent blends designated C, I, and J, show more potential in multi-contaminant removal than the individual solvents do.

Swell Index of Plastics

Some plastics are not affected by solvents; other plastics are affected in varying degrees. If a polymer is crosslinked, as are plastics derived from thermosetting resins, or is highly crystalline, solvency will be less likely to occur. An amorphous or loosely structured plastic would probably be soluble in several solvents.

Where plastics are substrates, solvents selected to remove contaminants must not dissolve the plastic or cause crazing of the surface. Swell index is a measure of the effects of solvents on plastics. A small, weighed amount (1-2 grams) of plastic is placed in a vial with the solvent being investigated. In 24 hours, the plastic sample (if it hasn't dissolved) is reweighed to determine the extent of solvent absorption. The percentage increase in weight is defined as the swell index.

Swell index data on a variety of thermoplastic and thermosetting plastics, including a glass-filled printed circuit board laminate (Tables 4 and 5), when used with contaminant solvency (Tables 1 and 3), provide for solvent selection best suited for a particular application. For example, if the plastic being used is sensitive to moderate hydrogen bonding solvents, then it may be necessary to use a weak hydrogen bonding solvent to remove contaminants. Trichloroethylene is a good solvent for removing contaminants, but it may also be a good solvent for several plastics as well. In contrast, isopropyl alcohol is quite often recommended for cleaning solvent sensitive plastics, since it doesn't attack the plastic. By the same token, its contaminant removal capability is limited.

Text continued on page 15

Table 2. Solvent Blend Formulations

Solvent Blend Designation	Composition	Percent by Volume
A	Methylchloroform Vinyltrichloride	50 50
B	n-Butyl acetate Isopropyl alcohol	50 50
C	Methylchloroform n-Butyl acetate Trichloroethylene Isopropyl alcohol	17 33 33 17
D	n-Butyl acetate Acetone 2-Ethylhexylchloride Vinyltrichloride	25 25 25 25
E	Acetone Vinyltrichloride Methylchloroform Cyclohexane Isopropyl alcohol	20 20 20 20 20
F	Methylchloroform n-Butyl acetate 2-Ethylhexylacetate	33 33 33
G	Methylchloroform n-Butylacetate Trichloroethylene	33 33 33
H	Perchloroethylene Methylenechloride Methylchloroform	50 20 30
I	Methylchloroform Methylenechloride	60 40
J	Methylchloroform Methylenechloride n-Butylacetate	38 48 14

Table 3. Effects of Solvent Blends on Contaminants*
 (Relative Ease of Removal of Contaminants
 by Solvent Blends)

Contaminants	Solvent Blend Designation**										
	A	B	C	D	E	F	G	H	I	J	
Solder Flux Types											
Abietic Acid	B	B	B	C	A	C	A	C	A	B	
Stearic Acid	B	A	A	C	B	A	C	A	B	A	
Machine Oil	A	C	B	C	C	C	A	A	A	B	
Photo Resist	C	B	A	B	B	C	C	C	C	C	
Spray Coating	C	B	A	B	C	C	A	B	B	B	
Fingerprint	B	C	B	C	B	B	B	A	B	A	
Hand Lotion	A	C	B	A	C	B	B	A	A	B	
Detergent	B	C	B	C	C	B	A	C	B	B	
Mold Release (Carnauba Wax)	C	C	C	C	C	C	C	C	C	C	
Grease	C	B	C	C	C	C	C	C	A	A	
Silicone Grease	C	C	C	C	C	C	C	C	C	C	

*Levels of contaminant solubility based on Meseran (ERA Systems Inc., Chattanooga, Tennessee) values after solvent rinsing.

**Refers to Table 2

A = Contaminant effectively removed (16 or less Meseran units)

B = Partly soluble. Longer rinse times should improve contaminant removal (17 to 99 Meseran units)

C = Limited contaminant solubility in solvent (greater than 100 Meseran units)

Table 4. Effects of Solvents on Plastics* (Showing Relative Solvency by Solvent Series)

Plastics	Hydrogen Bonding Class												Strong		
	Weak				Moderate				Strong						
	Hep-tane	2-Ethyl Hexyl Chloride	Trichloro-trifluoro-ethane	Methyl-1-Chloro-form	Toluene	Tri-chloro-ethylene	Perchloro-ethylene	Methylene-Chloride	Vinyl Chloride	2-Ethyl Hexyl Acetate	n-Butyl Acetate	Cello-solve	Acetone	Cyclo-hexanone	Isopropyl Alcohol
Teflon (1)	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Polyethylene	1	1	1	1	2	2	2	2	1	1	1	1	1	1	
Polyvinyl-chloride	1	1	1	1	2	3	1	5	4	2	4	2	4	5	
Nylon	1	1	1	1	1	1	1	2	1	1	1	1	1	1	
Acrylic	1	1	1	1	5	1	5	5	5	1	5	5	5	1	
Polystyrene	1	5	1	5	5	5	5	5	5	5	5	5	5	1	
Cellulose Acetate	1	1	1	2	2	3	1	5	5	1	3	5	5	2	
Mylar (1)	1	2	1	1	2	1	2	2	2	1	1	1	2	1	
Polyphenyl-sulfide	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Polycarbonate	1	1	3	3	5	2	5	5	1	3	3	3	5	1	
Phenoxy (2)	1	2	3	2	4	1	5	5	1	3	5	5	5	1	
Diallyl-phthalate	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Phenolic	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
Polyphenylene Oxide	1	2	1	5	5	5	5	5	2	3	3	3	4	1	
ABS	3	1	4	4	5	3	5	5	1	5	5	5	5	1	
Urethane	2	3	2	3	3	4	3	4	4	2	3	3	3	2	
Microballoen-filled Epoxy	1	1	1	1	2	1	2	1	5	3	2	1	2	1	
Polyester	1	1	1	1	1	1	1	2	1	1	1	1	1	1	
Kapton (1)	1	1	1	1	2	1	2	1	3	3	1	1	2	1	
Polyulfide	1	1	1	3	4	4	3	4	4	1	3	3	4	1	
Printed Circuit Board Laminato	1	1	1	1	1	1	1	1	1	1	1	1	1	1	

Levels of plastic solubility are based on percent swell in 24 hours.

*1. Little or no solvent absorption (swell equals less than 1 percent)

2. Slight absorption of solvent (swell equals 1 to 10 percent)

3. Moderate absorption of solvent (swell equals 11 to 19 percent)

4. Excessive solvent absorption (swell equals greater than 50 percent)

(1) Trade name of product of E. I. du Pont de Nemours

(2) Trade name of product of Union Carbide

Table 5. Effects of Solvent Blends on Plastics*
(Showing Relative Solvency, by Solvent)

Plastics	Solvent Blend Designation**									
	A	B	C	D	E	F	G	H	I	J
Teflon (1)	1	1	1	1	1	1	1	1	1	1
Polyethylene	2	1	2	1	1	1	2	2	2	2
Polyvinylchloride	3	2	2	3	3	2	2	3	4	4
Nylon	1	1	1	1	1	1	1	1	1	1
Acrylic	5	1	5	5	5	1	5	5	5	5
Polystyrene	5	5	5	5	5	5	5	5	5	5
Cellulose Acetate	4	3	3	3	4	1	3	3	3	3
Mylar (1)	1	1	1	1	1	1	1	1	2	2
Polyphenylene sulfide	1	1	1	1	1	1	1	1	1	1
Polycarbonate	5	1	3	3	3	2	3	5	5	5
Phenoxy (2)	5	5	5	5	5	2	5	3	5	5
Diallylphthalate	1	1	1	1	1	1	1	1	1	1
Phenolic	1	1	1	1	1	1	1	1	1	1
Polyphenylene Oxide	5	1	4	3	3	2	4	5	5	5
ABS	5	2	4	5	5	3	4	5	5	5
Urethane	4	3	4	3	4	3	4	4	4	4
Microballoon Filled Epoxy	1	1	1	1	2	1	1	1	2	2
Polyester	1	1	1	1	1	1	1	1	1	1
Kapton (1)	1	1	1	2	1	1	1	2	2	2
Polysulfide	4	2	3	3	3	2	4	3	4	4
Printed Circuit Board Laminate	1	1	1	1	1	1	1	1	2	1

Levels of plastic solubility are based on percent swell in 24 hours.

*1. Little or no solvent absorption (swell equals less than 1 percent)
 2. Slight absorption of solvent (swell equals 1 to 10 percent)
 3. Moderate absorption of solvent (swell equals 11 to 49 percent)
 4. Excessive solvent absorption (swell equals greater than 50 percent)
 5. Plastic dissolved partially or completely in solvent.

(1) Trade name of product of E. I. du Pont de Nemours.
 (2) Trade name of product of Union Carbide.

**Refer to Table 2.

ACCOMPLISHMENTS

Selection of solvent or solvent blends can now be made to remove specific (organic residue) contaminants without damaging plastics using compatibility charts established. Selective solvent blending based on solubility parameter principles has been demonstrated to be more effective than individual solvents in variety type contaminant removal.

Solubility parameter technology and evaporative rate analysis have been used to characterize individual contaminants as well as to determine the best solvents to be used for their removal from a substrate.

FUTURE WORK

Some contaminants take longer to remove than others, depending upon the solvents being used. Process efficiency of vapor degreasing, ultrasonic cleaning, and gas plasma cleaning will be studied for comparison with the rinsing technique as described in this report.

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¹Deleted.

²L. C. Jackson, *Comparison of Methods for Cleaning Contaminated Surfaces* (Topical Report). UNCLASSIFIED, Bendix Kansas City: BDX-613-1048, March, 1974.

³L. C. Jackson, *Solubility Parameters and Evaporation Rate Analysis in Organic Residue Characterization* (Topical Report). UNCLASSIFIED. Bendix Kansas City: BDX-613-1099, March, 1974.

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